

**A NEW AND MILD ACCESS TO N-FUNCTIONALIZED FORMAMIDO AND  
THIOFORMAMIDO COMPOUNDS USING HYPERVALENT SILICON HYDRIDES**

Robert J.P. CORRIU\*, Gérard F. LANNEAU, Myriam PERROT-PETTA  
and VIMAL Deep MEHTA

Université des Sciences et Techniques du Languedoc  
Institut de Chimie Fine, associé au CNRS - Case 007  
Place Eugène Bataillon - 34095 MONTPELLIER cédex 5 (FRANCE)

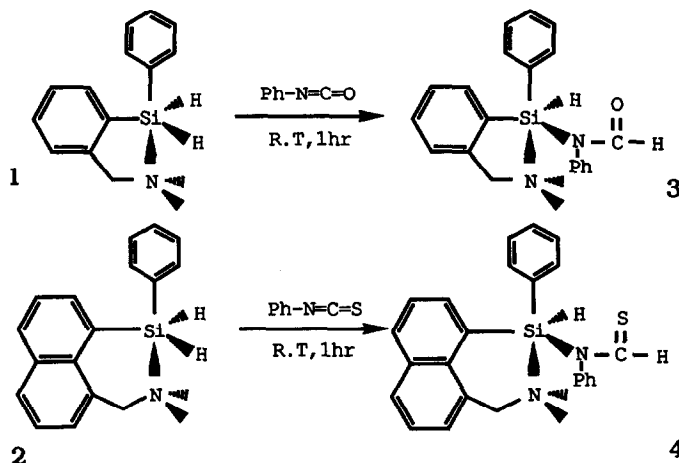
**Summary :** Hydrosilylation of isocyanates and isothiocyanates is achieved easily using hypervalent difunctional organosilanes. Treatment of the adducts thus obtained through one pot addition of electrophiles gives highly functionalized formamides and N-acylthioformamides.

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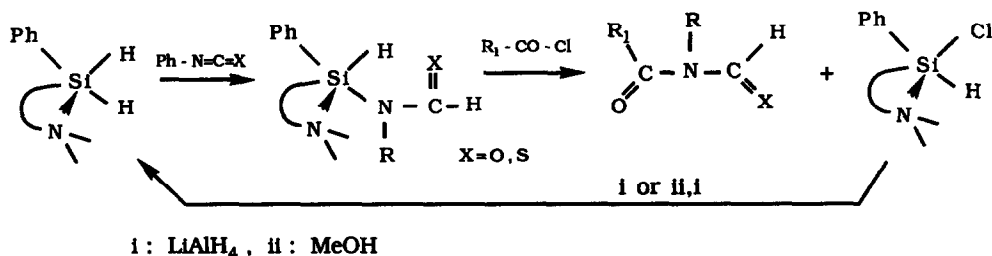
Not many methods are available to prepare N-acylformamides<sup>1</sup> and only one paper deals with the preparation of N-acylthioformamides.<sup>2</sup> Ojima has reported the hydrosilylation of isocyanates in the presence of catalysts at high temperature.<sup>3</sup> The cleavage of these amidosilanes with acid chlorides is to our knowledge the method of choice for the preparation of N-acylformamides in neutral conditions. The drawback of this process is the temperature conditions needed for the first step, *i.e.* the hydrosilylation of isocyanates. Isothiocyanates do not undergo hydrosilylation in the same reaction conditions.

The high reactivity of pentacoordinated organosilanes is now well established.<sup>4</sup> Neutral pentacoordinated hydrogensilanes have efficiently been used for reduction of aldehydes and ketones.<sup>5</sup> Acids have been reduced into aldehydes<sup>6</sup> and a highly selective Rosenmund type reduction of acid chlorides has been described.<sup>7</sup> Hypervalent silicon hydrides have also been found to be reactive towards CO<sub>2</sub>, CS<sub>2</sub>. Carbon dioxide has been converted into formaldehyde by insertion into the Si - H bond of a pentacoordinated organosilane, followed by decomposition of the product under mild conditions.<sup>8</sup> The CS<sub>2</sub> insertion intermediate decomposes at room temperature to give the first isolable silanethione.<sup>9</sup>

Here, we describe the reactivity of neutral pentacoordinated difunctional organosilanes towards two other heterocumulenes, isocyanates and isothiocyanates, and the synthetic utility of the adducts obtained. The pentacoordinated hydrogenosilanes react faster than the corresponding tetracoordinated species, without the requirement of added catalyst, as shown in the equations below.

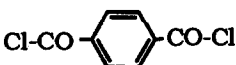
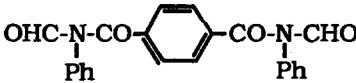
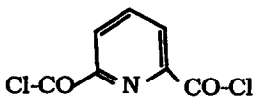
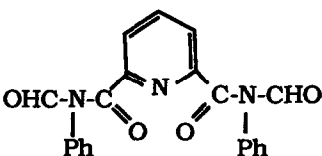
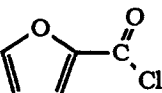
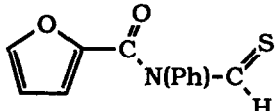
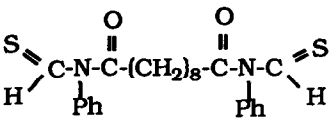
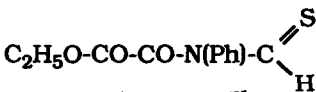
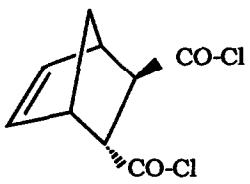
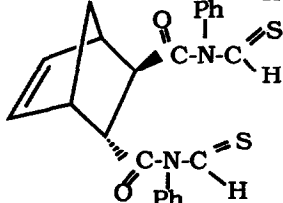
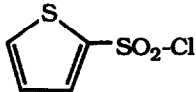
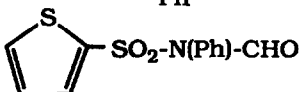
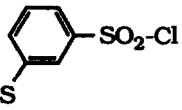
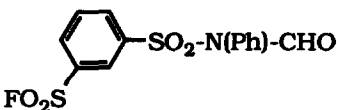


The (thio)formamido moieties react with weak electrophiles, affording a large variety of functionalized organic substances (Table).



The dihydrogenosilanes are easily obtained through orthometallation of dimethylaminoaryl compounds with *n*BuLi/hexane/Et<sub>2</sub>O and further coupling with PhSiH<sub>3</sub><sup>10</sup>. After purification by distillation (1) or crystallisation (2), they are treated with the stoichiometric amount of heterocumulene. As an example, 1 is treated with Ph-N=C=O in CCl<sub>4</sub> at room temperature giving in almost quantitative yield the corresponding silylformamide after 50-60 min. The one pot addition of acid chloride results in the formation of N-acylformamide and chlorosilane, in 20-30 min. N-acylformamides were easily separated from chlorosilane either by direct filtration from the reaction mixture or by flash column chromatography on silica-gel using CH<sub>2</sub>Cl<sub>2</sub> as eluant. The chlorosilanes were eventually recycled by reduction with LiAlH<sub>4</sub>, Et<sub>2</sub>O either directly or after methanolysis (excess of methanol). The structures to N-acylformamides 11 were assigned on the basis of their <sup>1</sup>H NMR (δ<sub>CHO</sub> 9 - 10 ppm), <sup>13</sup>C NMR (δ<sub>CHO</sub>: 163 - 164

Table. Reaction of **3,4** with electrophiles.

Silane	Acid Chloride	Product	Yield
<b>3</b>	$\text{CH}_2=\text{CH}-\text{COCl}$	$\text{CH}_2=\text{CH}-\text{CO}-\text{N}(\text{Ph})-\text{CHO}$	72
<b>3</b>	$\text{C}_2\text{H}_5\text{O}-\text{CO}-\text{COCl}$	$\text{C}_2\text{H}_5\text{O}-\text{CO}-\text{CO}-\text{N}(\text{Ph})-\text{CHO}$	85
<b>3</b>	$\text{C}_2\text{H}_5-\text{S}-\text{COCl}$	$\text{C}_2\text{H}_5-\text{S}-\text{CO}-\text{N}(\text{Ph})-\text{CHO}$	80
<b>3</b>	$\text{Ph}-\text{O}-\text{CS}-\text{Cl}$	$\text{Ph}-\text{O}-\text{CS}-\text{N}(\text{Ph})-\text{CHO}$	69
<b>3</b>			85
<b>3</b>			80
<b>4</b>			70
<b>4</b>	$\text{Cl}-\text{CO}-(\text{CH}_2)_8-\text{CO}-\text{Cl}$		72
<b>4</b>	$\text{C}_2\text{H}_5\text{O}-\text{CO}-\text{CO}-\text{Cl}$		70
<b>4</b>			81
<b>3</b>			74
<b>3</b>			79

ppm ;  $J_{\text{CHO}}$  190 Hz ;  $\delta_{\text{C}} = 0$  171 - 173 ppm) and mass spectrum. Under similar experimental conditions, the reaction of 2 with Ph-N=C=S gave N-silylthioformamide 12 which was subsequently cleaved with acid chlorides. The structures of N-acylthioformamides were confirmed by  $^1\text{H}$  NMR ( $\delta_{\text{CHS}}$  : 10.3 - 11 ppm),  $^{13}\text{C}$  NMR ( $\delta_{\text{CHS}}$  : 194 - 197 ppm ;  $J_{\text{CHS}}$  190 Hz ;  $\delta_{\text{C}} = 0$  170 - 172 ppm) and mass spectroscopy.

The selectivity of the method has been demonstrated by several examples : esters, alkoxy or thioalkoxy substituents, heteroaryl groups and C = C double bonds remain unchanged. The method is also suitable for the conversion of dicarboxylic acid chlorides into corresponding diformamides.

As shown in the table, the methodology has been successfully extended to prepare other N-substituted formamides using sulfonyl chlorides as electrophiles.

#### References and notes

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- (11) The initial insertion reaction product is N-Silylformamide, 3, which undergoes 1,3 migration to give O-silylformamido moiety after long time. M. Perrot - Ph.D Thesis - Montpellier - November 1989.
- (12) Similarly to 3, the N-silylthioformamide 4 undergoes slow 1,3 migration to give unstable S-silylformamide, which is immediately decomposed to silanethione - Ref.9.